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## Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926081>

### Interesting Errors in Sulfur Chemistry, 3

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**To cite this Article** Senning, Alexander(1982) 'Interesting Errors in Sulfur Chemistry, 3', Journal of Sulfur Chemistry, 2: 4, 175 – 176

**To link to this Article:** DOI: 10.1080/01961778208082434

**URL:** <http://dx.doi.org/10.1080/01961778208082434>

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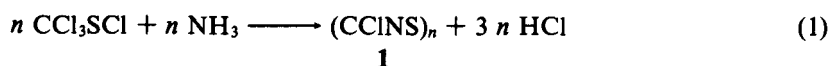
## INTERESTING ERRORS IN SULFUR CHEMISTRY, 3

ALEXANDER SENNING

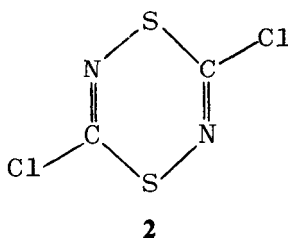
*Kemisk Institut, Aarhus Universitet, DK-8000 Århus C, Denmark*

### 3,6-DICHLORO-1,4,2,5-DITHIADIAZINE

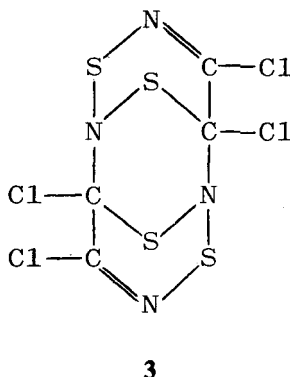
In 1963 it was found that trichloromethanesulfonyl chloride and ammonia could be made to react with elimination of hydrogen chloride according to (1):<sup>1</sup>



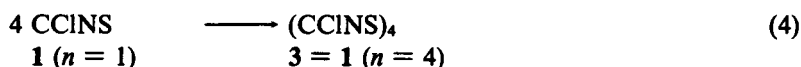
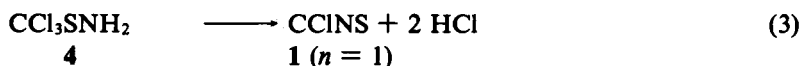
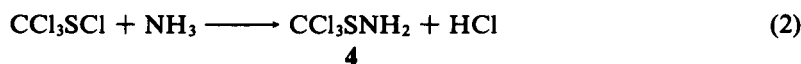
By standard procedures, including an ebullioscopic molecular weight determination, the product of the reaction, m.p. 200.5–201.5°C, was assigned the structure of 3,6-dichloro-1,4,2,5-dithiadiazine **2** equivalent to **1** ( $n = 2$ ).



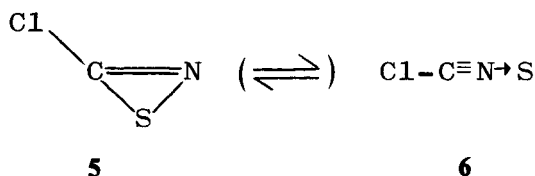
Three years later the compound originally regarded as **2** was subjected to further chemical<sup>2</sup> and crystallographic<sup>3</sup> scrutiny and unequivocally shown to possess the structure of 2,3,7,8-tetrachloro-5,10,11,12-tetrathia-1,4,6,9-tetraazatricyclo-[5.3.1.1<sup>2,6</sup>]dodeca-3,8-diene **3** equivalent to **1** ( $n = 4$ ).



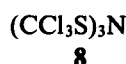
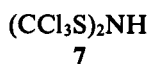
An obvious way to rationalize the formation of **3** (which in all probability must involve **2** as a transient intermediate) is to assume a reaction path via the sulfenamide **4** and the monomer **1** ( $n = 1$ ) which then oligomerizes in more or less discrete steps:<sup>2</sup>



The intermediate **1** ( $n = 1$ ) is probably 3-chlorothiazirine **5** or cyanogen chloride N-sulfide **6** or an equilibrating mixture of both:



The relationship between nitrile N-sulfides and thiaziridines has been investigated in depth.<sup>4</sup> Though the postulated intermediate **4** was subsequently synthesized according to (2) and fully characterized<sup>5</sup> (as were the related compounds **7**<sup>6</sup> and **8**<sup>6</sup>) **2** has eluded synthesis up to the present day and no more light has been shed upon the intriguing reaction (1).



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